Turbulent Mixing with Multiple Second-Order Chemical Reactions

A molecular-based statistical simulation program was developed to study the covariance terms involved in the mass balance equations for complex chemical reactions during mixing. Several closure theories were compared to the simulations and available experimental data. The simple closure by Brodkey and Lewalle was found to be an extension of Toor's analysis applied to two reactions. This closure does not satisfy the molar fluctuation balance equation and was found only to represent the high Reynolds number data of Li and Toor. This result led to examining other possible closures which were based on Damkoehler numbers, reaction rate constant ratios, and limiting forms of the covariance term. These closures also were inadequate. The second reaction's covariance term varied from the product of the average values for each component to the Brodkey and Lewalle value for the range of Reynolds numbers considered.

Thomas G. Heeb
Robert S. Brodkey
Department of Chemical Engineering
Ohio State University
Columbus, OH 43210

Introduction

Chemical reactor design is a major area of research. The design is relatively simple for laminar flow, but difficult for turbulent flow. Unfortunately, the majority of reactors operate in the turbulent flow regime. Turbulent flow occurs because of either the necessity of high heat and mass transfer rates to control temperature or high throughputs for economic reasons. In spite of the need for turbulent design methods, they are only available for the simple single step reactions of the type:

$$A + B \xrightarrow{k} C \tag{1}$$

The complexity for parallel reactions such as

$$\begin{aligned} A + B &\xrightarrow{k_1} R \\ A + C &\xrightarrow{k_2} S \end{aligned} \tag{2}$$

or the even more complex simultaneous-consecutive reactions such as

$$\begin{aligned} A + B &\xrightarrow{k_1} R \\ R + B &\xrightarrow{k_2} s \end{aligned} \tag{3}$$

has prevented researchers from suggesting accurate closure methods for modeling. Of considerable importance is the influence of turbulent mixing on the selectivity of chemical reactions when complex reactions (Eq. 2 or 3) are involved. This selectivity is associated with the optimization of an intermediate product (R) from the reaction at the expense of the final product (S), i.e., the ratio of R/S.

The closure for the single reaction (Eq. 1) was suggested by Toor (1969) and has become known as Toor's hypothesis. Further comments on this closure have been made by Leonard and Hill (1989) and by Kosaly (1987). Modeling using this closure was tested by direct experimentation on acid-base reactions in one idealized reactor design. The experimental conversion measurements were made by a heat balance using the heat of reaction (Mao and Toor, 1970, 1971; Vassilatos and Toor, 1965). The velocity field was measured by conventional anemometer methods and the conversion accurately predicted from these results by McKelvey et. al. (1975). Unfortunately,

---

Thomas Heeb is associated with Westreco Inc., Marysville, OH 43040. Correspondence concerning this paper should be addressed to R. S. Brodkey.

the heat balance technique cannot be used for the more complex reactions given by Eq. 2 or 3. There is no way to separate the contributions from the two steps. Bourne has developed a chemical reaction that can be used for very high reaction rate ratio for the simultaneous-consecutive reaction (Eq. 3). However, many commercial chemical reactions such as the initial stages of polymerization, combustion and air pollution are not in this class. Their reaction rate ratios are near unity.

Guidelines are needed to direct closure techniques. These techniques are a function of the kinetics of the reaction, diffusion of the species present, turbulent field, mean concentration, and variance of the reacting materials. Actual experiments with chemicals in turbulent reactors for complex chemical reactions have to date not been able to provide the guidelines needed. Experiments for certain ranges of the kinetic constants are currently impossible because the reaction with the desired kinetic ratios have not been found. However, our knowledge of turbulence and kinetics allows such experiments on a computer. Although there are limitations about the range of variables that can be run even on a supercomputer, guidelines can be obtained for reaction conditions of importance. Depending on the complexity and approach, information on higher moments, cross moments, multipoint moments, etc. can be obtained. As examples of such full simulations, rather than the model simulation done here, one can cite the work of Givi and McMurtry (1988) and Leonard and Hill (1989). With such information, reasonable hypotheses can be made to relate unknown terms to the mean concentration of the reacting materials and the turbulent field characteristics. Once accomplished, the closures can be used for modeling and design purposes. The current work was attempted to help gain a better understanding into basics of the multireaction turbulent mixing part of the design problem.

Reaction rate determines the extent to which a reaction system will show effects of turbulent mixing. Three ranges of rates were defined by Vassilatos and Toor (1965) and by Mao and Toor (1971). These were slow, rapid and very fast: very fast reactions had a rate constant greater than about 10^6 $m^3 \cdot kmol^{-1} \cdot s^{-1}$; slow was less than about 10^3 $m^3 \cdot kmol^{-1} \cdot s^{-1}$; and rapid was in between. The slow reaction is kinetically controlled and occurs when mixing is essentially complete before reaction occurs. The system is therefore essentially premixed. For this case, conversions depend only on the homogeneous reaction rate and the residence time distribution. The very fast reaction is controlled by the mixing rate since the reaction occurs almost instantaneously at the interface between segregated regions of components. This case requires additional information concerning the mixing, such as the intensity of segregation: a measure of the degree to which the multiple reactants are isolated in space. The rapid reaction condition is controlled jointly by chemical kinetics and mixing rates. This case requires all the information provided for the other two cases: both mixing and kinetics data.

Overview of areas of analysis

One approach to the turbulent mixing and reaction problem depends on solution of the Reynolds averaged, turbulent, mass balance equations. The problem is that the number of unknowns exceeds that of equations. Closure can be obtained from additional relationships, called "closures." With an adequate closure, the equations can be solved in theory at least. This work examines critically a closure proposed by Brodkey and Lewalle (1985) and evaluates alternative closures as well. A statistical simulation program was developed to determine the nature of the covariances and to determine how well various closures can predict the multiple reaction covariances.

Further comparisons were made between predictions using the closures and the experimental data of Li and Toor (1986). The analysis applied numerical integration techniques to the simultaneous mass balance and kinetic rate equations. The intensity of segregation or the covariance of the first reaction served as the measurable variable in most of the examined closures.

Review of turbulent flow reaction processes and methods of solution

Reactors are commonly either tubular flow reactors or stirred tank reactors. Procedures for the stirred tank reactor can be found in: Rao and Brodkey 1972; Klein et al. (1980); Paul and Treybal (1971); Nabholz et al. (1977); David and Villermaux (1975); Ghodsizadeh and Alder (1981); and Baldyga and Bourne (1984). Designs for tubular flow reactors are often based on the initial scale of mixing. Mixing may be single jet or multijet. Single-jet tubular reactors have been examined by Lee and Brodkey (1964) and by Singh and Toor (1974), for example. Multijet reactors have two different jet patterns. In an early design by Vassilatos and Toor (1965), the jets were arranged in an open square array packing. In the latter design, the tubes followed a close packed array (Amerja et al., 1976; Mao and Toor, 1970, 1971; Singh and Toor, 1974) to produce a flatter velocity profile across the reactor and to minimize the mixing between jets in the initial small recirculation region.

Physical models such as coalescence-redispersion, mass transfer between two slabs, lamellar stretching and interchange with the mean have been proposed to describe the turbulent mixing and reaction problem. All of these models have adjustable parameters which must be fitted to the experimental data. Such models do fit the series-parallel reaction data for which the closure models have failed. Thus, such models are the ones we use for design; however, they do not necessarily describe correctly the underlying physical reality of the mixing-reaction process. The procedure of using the Reynolds averaged equations together with a logical closure approximation is still desired. The need is, however, the closure. This paper has two parts, the second is finding possible closures and using the Reynolds averaged equations to make comparisons to the published experimental data. The first part is to establish such possible closures by using a stochastic simulation of a random turbulent-like mixing field (without net flow) in which reactive mixing occurs.

Statistical Theory of Turbulent Mixing

An extensive review of the statistical approach that uses the average equations and closures will not be given here; the specific papers already cited provide considerable detail. More general references are Brodkey (1967, 1975) and by Ulbrecht and Patterson (1985). The mixing is obtained through the intensity of segregation, I_s, which for pure mixing is taken as

$$I_s = \overline{ab}/\overline{(ab)}_o = \overline{ab}/A_o B_o \tag{4}$$

where the subscript o denotes an initial state. A_o and B_o are constant and equal to the equivalent initial mixed feed concentration of A and B. Equation 4 uses the same normalization as used by Brodkey and Lewalle (1985).

The analysis of importance for this work involves the simultaneous-consecutive reaction sequence (Eq. 3). This reaction is of interest because of the second covariance term and the selectivity of products. Brodkey and Lewalle (1985) proposed a closure relationship which allowed the mass continuity equations to be solved. They based their closure equation on results that they obtained from a simple stochastic simulation of a single two-cell mixing reaction system. Their suggested closure is

$$\overline{br} = \overline{ab}(\overline{R}/\overline{A}) \tag{5}$$

This closure needs further evaluation, since it is possible to show that it corresponds to the extension of Toor's hypothesis to both reactions. The derivation can be found in the dissertation by Heeb (1986) and is given here as appendix A. The procedure to generate this closure is basically the same as that for the $\overline{ab}$ continuity equation. If the closure is inadequate, then Toor's hypothesis is not valid for the second reaction in the two reaction case. It may still be valid for the first reaction. It can also be shown that the closure does not satisfy the overall balance equation for the fluctuating components (Heeb, 1986). This is shown in appendix B. The intensity of segregation, I_s given by Eq. 4, is a normalization. The $\overline{br}$ covariance is also normalized in all the figures in exactly the same way, i.e., with $\overline{(ab)_o} = A_oB_o$.

The crux of the simultaneous-consecutive reactive mixing problem is the evaluation of the covariance term $\overline{br}$ for closure. Even if Eq. 5 is inadequate, limits can be evaluated by assuming limiting forms of $\overline{br}$. These are zero, $B_o\overline{R}$ and $\overline{B}\,\overline{R}$. The limit of $\overline{br}$ equal zero was chosen since the r-fluctuations are initially small, while the b-fluctuations are large thus resulting in a small $\overline{br}$. As reaction proceeds, the r-fluctuations become large while the b-fluctuations become small again resulting in a small $\overline{br}$. The limit of $\overline{br}$ equal to $B_o\overline{R}$ is the maximum realistic average upper limit for the $\overline{br}$ covariance term. This occurs because B_o is constant and R initially increases as the first reaction proceeds and then decreases as the second reaction occurs. The limit of $\overline{br}$ equal to $\overline{B}\,\overline{R}$ is a more reasonable upper limit which allows the $\overline{br}$ covariance to change from increasing to decreasing as both $\overline{B}$ and $\overline{R}$ change. Other closures can be used which involve a change of sign. This would correspond to assuming premixed conditions for the $\overline{br}$ term.

Still another technique would be to use Damkoehler numbers to relate the $\overline{br}$ term to the $\overline{ab}$ term. The major problems with this technique are the definitions of the concentration and length scale that are used. However, these can be avoided if ratios are used. In such a case, it does not matter if the first or second Damkoehler number is used. Using the first Damkoehler number as the example gives

$$N_{Dm_{1,i}} = \frac{\text{Rate of Reaction } i}{\text{Convection Rate}} \tag{6}$$

One possible definition for the closure ratio would be to use average rates:

$$\frac{\overline{br}}{\overline{ab}} = \overline{\left(\frac{N_{Dm_{1,2}}}{N_{Dm_{1,1}}}\right)} = \frac{\text{Rate of Reaction 2}}{\text{Rate of Reaction 1}} = \frac{k_2\overline{R}}{k_1\overline{A}} \tag{7}$$

Another possible definition for the closure ratio would be

$$\frac{\overline{br}}{\overline{ab}} = \left(\frac{\overline{N_{Dm_{1,2}}}}{\overline{N_{Dm_{1,1}}}}\right) = \frac{\text{Rate of Reaction 2}}{\text{Rate of Reaction 1}} = \frac{k_2(\overline{B}\,\overline{R} + \overline{br})}{k_1(\overline{A}\,\overline{B} + \overline{ab})} \tag{8}$$

where the form of the rates for the second-order reaction can be found as Eqs. A9 and A10 for appendix A. Equation 7 when solved for $\overline{br}$ is equivalent to

$$\overline{br} = \overline{ab}(k_2\overline{B}\,\overline{R})/(k_1\overline{A}\,\overline{B} + k_1\overline{ab} - k_2\overline{ab}) \tag{9}$$

A list of closures tested is given in Table 1. Closure 1 is the Brodkey-Lewalle form, closure 12 is that given by Eq. 7, and closure 13 is Eq. 9. In the table are other possible relationships that can be obtained, if the convected component is assumed to be the average of the two reactant terms in the reaction expressions. These approximations were tried with both the first and second Damkoehler numbers. Additional relationships were

Table 1. Closure Forms

Closure No.	Equation Relating $\overline{br}$ to $\overline{ab}$ or I_s	
1	$\overline{br} = \overline{ab}\dfrac{\overline{R}}{\overline{A}}$	(5)
2	$\overline{br} = 0$	(10)
3	$\overline{br} = \overline{B}\,\overline{R}$	(11)
4	$\overline{br} = B_o\overline{R}$	(12)
5	$\overline{br} = -\,\overline{ab}\dfrac{\overline{R}}{\overline{A}}$	(13)
6	$\overline{br} = -\,\overline{ab}\dfrac{\overline{R}}{\overline{A}} \quad N_1 > 1$	(14)
	$\overline{br} = \overline{ab}\dfrac{\overline{R}}{\overline{A}} \quad N_1 < 1$	(15)
	$\overline{br} = 0 \quad N_1 = 0$	(16)
7	$\overline{br} = \overline{ab}\dfrac{\overline{R}}{\overline{A}} \quad N_2 > 1$	(17)
	$\overline{br} = -\,\overline{ab}\dfrac{\overline{R}}{\overline{A}} \quad N_2 < 1$	(18)
	$\overline{br} = 0 \quad N_2 = 0$	(19)
	where N_1 and N_2 are the Damkoehler numbers	
8	$\overline{br} = \overline{ab}\dfrac{\overline{R}}{\overline{B}}$	(20)
9	$\overline{br} = \overline{ab}\dfrac{\overline{R}}{\overline{A}}\overline{B}\,\overline{R}$	(21)
10	$\overline{br} = \overline{ab}\,N_{Dm_{1,2}}$	
	where the concentration was taken as $\overline{B}\,\overline{R}/[(\overline{B} + \overline{R})/2]$	(22)
11	$\overline{br} = \overline{ab}\dfrac{N_{Dm_{1,2}}}{N_{Dm_{1,1}}}$	
	where $N_{Dm_{1,2}}$ is the same as in Eq. 22 and $N_{Dm_{1,1}}$ has the concentration as $\overline{A}\,\overline{B}/[(\overline{A} + \overline{B})/2]$	(23)
12	$\overline{br} = \overline{ab} = \overline{\left(\dfrac{N_{Dm_{1,2}}}{N_{Dm_{1,1}}}\right)} = \dfrac{k_2\overline{R}}{k_1\overline{A}}\overline{ab}$	(7)
13	$\overline{br} = (\overline{ab}k_2\overline{B}\,\overline{R})/(k_1\overline{A}\,\overline{B} + k_1\overline{ab} - k_2\overline{ab})$	(9)
14	$\overline{br} = \overline{ab}\dfrac{\overline{R}}{\overline{A}}K$	(24)
	where K is a function of Reynolds number	

generated which are combinations of previously derived forms; as an example, closures 6 and 7 were based on changing from the Brodkey-Lewalle closure to a negative Brodkey-Lewalle closure to zero depending on the value of the Damkoehler number ratio. No second Damkoehler number closures are given since the results were indistinguishable from the first Damkoehler number results.

Since the completion of the basic work for this publication (Heeb, 1986), an important contribution has been made by Dutta and Tarbell (1989). These authors show the general inadequacy of closures 1 and 2 in Table 1, as did Li and Torr (1986). They also suggested alternate closures, based on limiting forms of model representations, such as the three- and four-environment models. These latter suggestions were unknown to us at the time of this work. They did not consider most of the closure variations cited in Table 1, especially those dependent on the Damkoehler numbers.

Statistical Simulation Analysis

The closure given by Eq. 5 was first established by using a simplistic stochastic reaction cell model (Brodkey and Lewalle, 1985). The present work was undertaken to improve the cell geometry, to test the influence of kinetics and mutual diffusion of the species involved on the closure, and to established improved closures.

Assumptions of the analysis technique

The statistical simulation analysis was tested by setting up a cell model to determine if the statistics of real mixing problems could be generated by such a limited model. The model used was a static one with no flow involved. The model allowed random events such as mass transfer and reaction to occur. The model represented the fluid as cells or clumps of molecules. The number of components initially was set in a cell for each trial. Many assumptions were needed to evaluate the model:

- Binary equimolar mass transfer happened between cells when diffusion occurred.
- One event, such as one reaction or one equimolar counterdiffusion between cells, occurred per cell per time step.
- Reactions always involved at least one of the two main reactants.
- Probabilities were equated to the fraction represented by the specific events occurrence divided by all events occurrence value.
- Reactions were considered to be bimolecular second-order elementary reactions.
- All rate constants were normalized with the diffusivity of the first main reactant as in the second Damkoehler number (i.e., k_1/D_1) and the ratio has units of m · kmol^{-1}.
- The diffusivity of the first and second reactant were considered equal.
- All other diffusivities were calculated using Le Bas volume method of estimating diffusivities or were set equal to the diffusivity of the first component.
- Mass transfer occurred only between cells which had common borders.
- Cells remained in the same configuration throughout the test period.

The model could be used to examine closures by using the closure in the simulation routines at the appropriate places. The model allowed statistics, such as overall averages and covariances, to be determined for various input conditions. Time averages at a point were approximated by two techniques: ensemble and volume averaging. The two techniques differ in the assumptions used to approximate the true time average. Several modified methods of circulating the component averages and fluctuations were incorporated into the model simulation routines. These were

- The Rao and Brodkey (1972) method of closure which reduces the component averages by the averge amount of each component in the opposite type of cell
- Reduction of the number of cells to a mass equivalent two-cell system (degeneration) followed by regular calculation methods
- Subtraction of the minimum amount of each component from every cell or from the calculated average (omission) before regular calculations are made
- Degeneration with omission before regular calculations
- Regular calculations without any changes to the system.

The time steps used in the model were considered to be the time required for one event, such as one reaction or one equimolar counterdiffusion to occur in each cell. The events considered are

- Binary diffusion between two cells
- Reaction in a cell
- No change to a cell.

The model assumes that each cell has one of these events occurring each time interval. Once a cell event occurs, it is no longer available until a new interval is started. The assumption assures that each cell is considered only during each interval. If diffusion occurs, then two cells are involved and both cells are no longer available until a new interval starts. The size of the time interval is considered an approximation for the time required for a real mixing system to change, but the scale or proportionality constant relating this to the time of the real mixing system is unknown. Thus, there is no way to compare such a stochastic simulation to actual measurements of mixing. The value of the simulation is as a model for turbulent mixing where it might provide insight into improving closures.

Methods of averaging

The statistical simulation model is used to generate statistics. The techniques used to calculate the averages and fluctuation components of the instantaneous concentrations need to be examined because different definitions could apply to the intensity of segregation and closures. Danckwerts defined the intensity of segregation using initially pure components. This definition requires that all the cells have the component amounts adjusted to amounts in cells containing only one of the two initial reactants. The adjustment is done by subtracting the lesser amount of each of the two initial reactants from all cells. Different definitions for some closures have been demonstrated by Rao and Brodkey (1972). They have redefined the averages in the I_s expression to account for the initially impure cells (cells which contain both types of components). They obtained their result by examination of a recycle system.

Two views of averaging can be used: the ensemble average of many simulations at equal time steps and the volume average of many cells or points for one simulation. The ensemble averaging technique uses the ergodic assumption that the ensemble average from many runs is equivalent to the time average at the same location. This averaging technique is shown by:

$$\langle A \rangle = \overline{A} \quad \text{Ergodic Assumption} \tag{25}$$

$$\langle A \rangle = \sum_j A_j / J \quad \text{Ensemble Average} \tag{26}$$

$$\overline{A} = \sum_t A_t / T \quad \text{Time Average} \tag{27}$$

where A_j is a value of A for the jth simulation, J is the total number of simulations, A_t is the value of A at time t, and T is the total time. The ergodic assumption allows each simulation to represent the instantaneous concentration of the components, and the average value is then calculated from all the simulations.

The volume averaging technique requires just one simulation with many cells. This technique assumes that each cell is equivalent to a time measurement. Therefore, the volume average at a specific time step is equivalent to the time average at the same position. The underlying assumption that each time measurment is represented by one cell requires that the cells are assumed independent as the time measurements. This technique is shown by:

$$A_v = \overline{A} \quad \text{Volume Assumption} \tag{28}$$

$$A_v = \sum_x A_x / N \quad \text{Volume Average} \tag{29}$$

where A_v is the volume average at a time step, and N is the total number of cells in the volume. Thus, this technique utilizes each cell as a time measurement and calculates the corresponding averages and fluctuations from the cells' component values. Another assumption made by the volume averaging technique is that each cell has the same volume or size as the measuring probe and that the probe volume measures only one cell at any one time. The ensemble averaging technique utilizes a random selection of each simulations' cells. This technique uses only one cell per run to approximate the instantaneous component values since fluctuations from the averages cannot be determined if all the cells are used. Thus, both cases presume that the concentration of a component as a function of time can be approximated by cell values at the same position.

Discussion of the simulation computer program

Details of the simulation computer program can be found in the dissertation by Heeb (1986) and is reviewed in Figure 1. The simulation was written in modular form with input, base cell, configuration (two- or three-dimensional, two-cell, multirun, multicell are selected here), event determining, concentration setting, statistics and closure equations routines. The details will not be given here; however, a few key points need to be made.

The base cell routine checks to ensure that the chosen cell is available for use before completion. The configuration routine determines which cells share a common border. The event-determining routine calculates the binary mass transfer rates between the base cell and all available common border cells. The reaction rates are calculated for the base cell. The rates are summed and fractions calculated which represent the occurrence probabilities of the events such as reaction or mass transfer. The event to occur is chosen by random selection using a random number generator. If reaction occurs, then the routine can include a diluent effect which allows reactants to be in the same cell and not react. In this case, the reactants are too distant due to the large volume of the solvent or diluent. The diluent effect is also randomly selected based on the amount of each component present in the base cell. If a reaction or the diluent effect was selected, then this routine is completed. If diffusion occurs, however, then the second diffusing component must be selected. The selection is done by reevaluating the mass transfer rates of the remaining components of the two cells involved. Control is passed next to the concentration setting routine which adjusts the amount of the specific components for the desired event that was chosen to occur. The program then calls the routine which sets the current base cell unavailable; and if mixing occurred, then the complimentary mixing cell also becomes unavailable for further use until a new time interval is started. The program returns to the base routine to choose another base cell, and the iteration continues until every cell becomes unavailable.

The program then branches depending on the type of approximation used to express the time average at a point. The first path is the ensemble path which prints output (when desired) and then increments the time step. After all time steps occur, this path requires resimulation of the same system with different random number generator seeds. This method runs the simulation several times and calculates the output data of the simulations at selected time steps. The second path involves volume averaging which assumes that a single simulation produces cells which are equivalent to individual measurements at a point. Thus, the cells can be averaged to produce the time average at a point. This path does calculations at the current time step and then increments the time step before looping back.

The program provides outputs such as description of the events chosen, a picture of the cells at each time step, summation of the averaged terms from continuity and closure information about the values of the second-order covariance terms.

Simulation input conditions and comparisons of models

Clearly, the simplest simulation would be the two-cell model, followed by the multirun model. The most realistic would be the multicell model. First, it is necessary to show that the multirun and multicell models approach a steady-state average. We need to determine how many time steps are necessary to arrive at a reasonable result. Then, with specific input conditions, comparisons can be made to judge what level of complexity is required and to establish the adequacy of the simpler two-cell approach.

The range of input conditions varied over values of k_1/k_2 from 1 to 2,000 and of k_1/D_1 from 10^3 to 10^{16} m · kmol^{-1} for both equal and unequal diffusivities. An attempt was made to cover the entire range from slow through rapid to very fast reactions. The experimental results available were at a kinetic constant ratio of 2,000, the top of the range used. With a value of D of 1.24×10^{-9} m^2 · s^{-1}, the k_1/D_1 ratio would be 5.9×10^{15} m · kmol^{-1}, close to the upper limit of 10^{16} used in the simulations. A kinetic ratio (k_1/k_2) of 1 was used to simulate the first few reactions of polymerization with a single rate constant for which up to nine simultaneous-consecutive reactions were considered.

Statistically many cells should be used to determine if the two-cell volume average simulation technique yields valid information. The ensemble average technique involved many computer runs of two-cell simulations. The number used was 200.

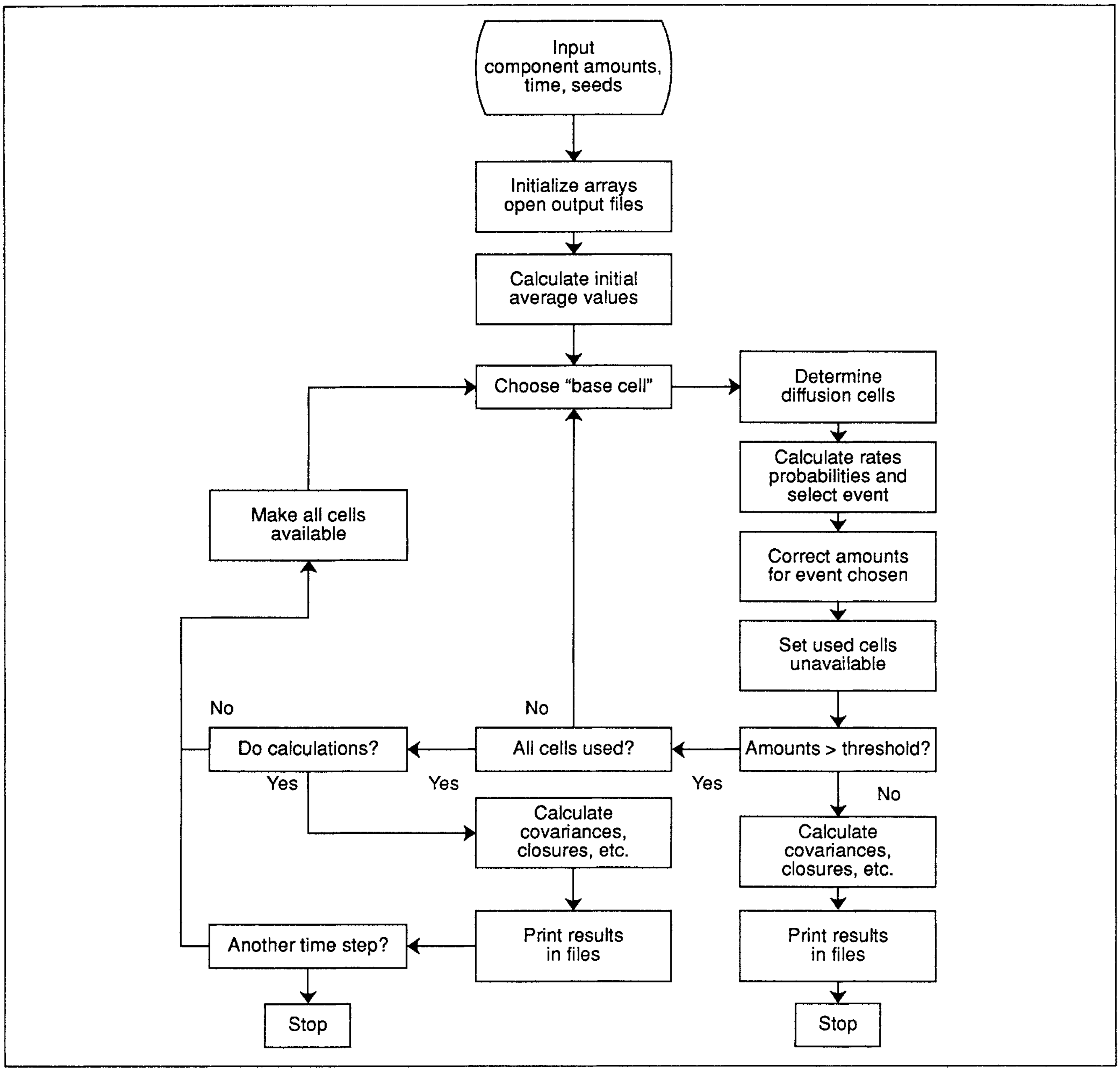

Figure 1. Simulation computer program flow diagram.

Random selection determined which of the two cells per run (with the requirement that the sum of each type of cell be the same) were used in the calculations. Thus for 200 simulations an average was obtained from two hundred cells. This type of analysis was performed to define the number of runs necessary to yield meaningful results.

Figures 2 and 3 show that the covariance terms have settled to near the final value when the number of runs is between 50 and 100. Figures 4 and 5 show the covariances as a function of time. Recall that the $\overline{br}$ covariance is normalized in the same manner as I_s. The $\overline{br}$ covariance curves are much smoother than the two-cell volume averaged curves that are shown in the dissertation of Heeb (1986) and not repeated here. The general shapes and magnitude of the individual curves confirmed the results from the two-cell volume averaged simulations. Thus if only general results are desired, then computer time can be saved by using a two-cell volume-averaging simulation over a multirun simulation.

The more detailed and certainly more realistic multicell simulation uses the volume-averaging technique. Figures 6 and 7 show the effect of the number of cells on the covariance terms. The volume-averaging technique is more variable at the 64-cell level compared to the multirun case at the 64-run level. Figures 8 and 9 show the covariances for the 64-cell model (parallel to Figures 4 and 5). Only minor differences were observed when a test run was made at 196 cells (Heeb, 1986). The results of the simulations indicate that increasing the k_1/k_2 ratio (from region A and B for $k_1/D_1 = 10^7$, from region C to D for $k_1/D_1 = 10^{10}$ and from region E to F for $k_1/D_1 = 10^{16}$) slightly decreases I_s and makes $\overline{br}$ approach zero for all possible

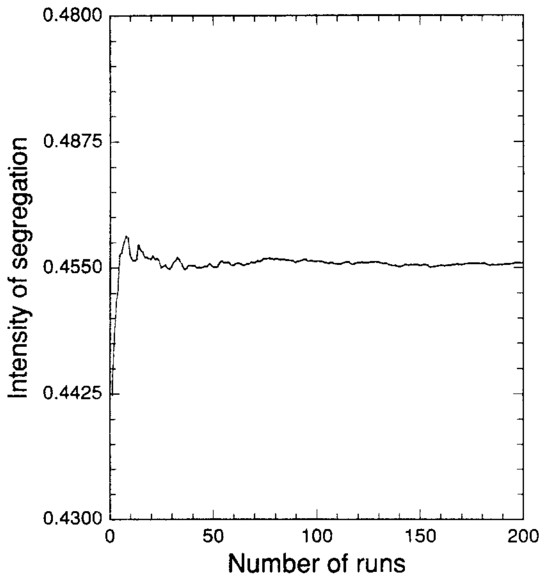

Figure 2. Intensity of segregation variation in the multirun simulation for $k_1/D_1 = 10^{16}$ and $k_1/k_2 = 2{,}000$.

controlling mechanisms. Thus, an increasing kinetic ratio causes I_s and $\overline{br}$ to approach zero. This result is expected for the $\overline{br}$ covariance. As the kinetic ratio increases, the amount of R consumed in the second reaction decreases causing the amount of R in each cell to be about equal. This happens since equimolar counterdiffusion was assumed and the first reaction should occur at equivalent rates in both types of cells. The decrease of I_s is equivalent to a decrease in $\overline{ab}$. This is expected, since more reactions involving A and B will occur and therefore the amount of both should decrease faster than at equal kinetics. Thus, I_s should decrease with an increasing kinetic ratio. The maximum difference in the I_s curves is about 0.05 or 25% error based on the lower kinetic ratio. The maximum difference in the $\overline{br}$ curves is also 0.05 which corresponds to about 85% error based on the lower kinetic ratio. Thus, the difference has approximately the same absolute size for both covariances. The effect is shown to be much greater on the $\overline{br}$ covariance, since the absolute size of the $\overline{br}$ covariance is so much less than the absolute size of the $\overline{ab}$ covariance (I_s).

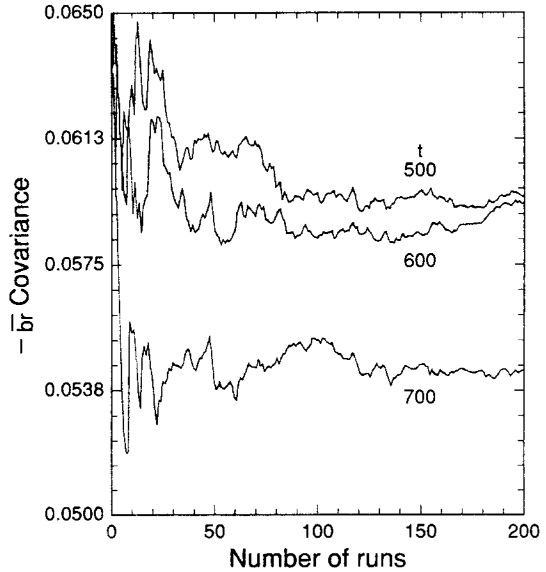

Figure 3. Normalized $\overline{br}$ variation in the multirun simulation for $k_1/D_1 = 10^{16}$ and $k_1/k_2 = 2{,}000$.

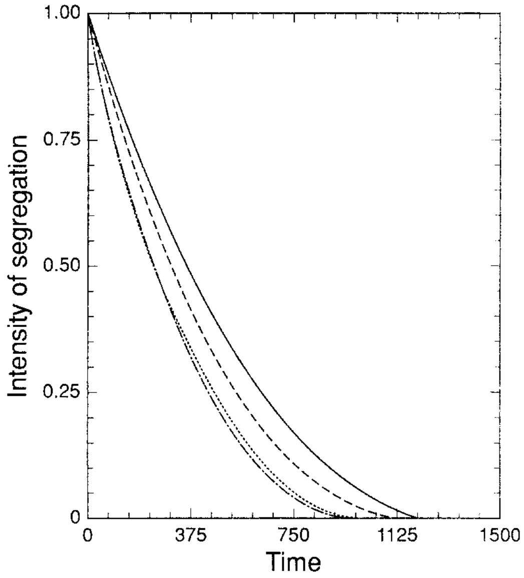

Figure 4. Intensity of segregation variation with time in multirun simulation.

For $k_1/D_1 = 10^7$ and $k_1/k_2 = 2{,}000$ (-·-·-) or $k_1/k_2 = 1$ (· · · · ·); for $k_1/D_1 = 10^{10}$ and $k_1/k_2 = 2{,}000$ (-----) or $k_1/k_2 = 1$ (solid line); for $k_1/D_1 = 10^{16}$ and $k_1/k_2 = 1$ or 2,000 with or without equal D

A short summary of the results is given in Table 2. Some of the results reported by Heeb (1986) for the two-cell simulations

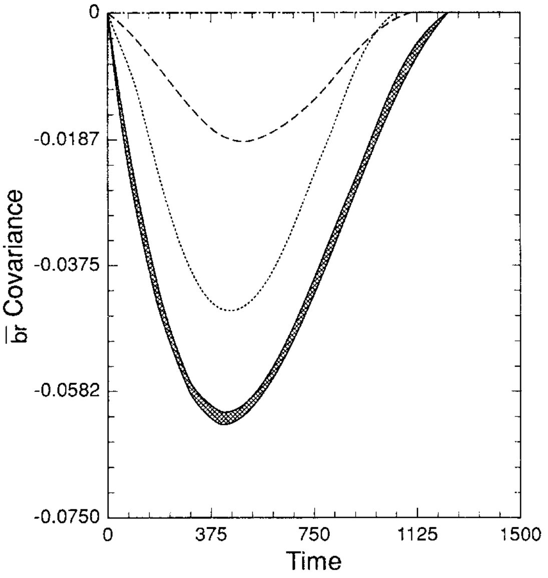

Figure 5. Normalized $\overline{br}$ variation with time in multirun simulation.

For $k_1/D_1 = 10^7$ and $k_1/kBO_2 = 2{,}000$ (-·-·-) or $k_1/k_2 = 1$ (· · · · ·); for $k_1/D_1 = 10^{10}$ and $k_1/k_2 = 2{,}000$ (-----) or $k_1/k_2 = 1$ (crossed area); for $k_1/D_1 = 10^{16}$ and $k_1/k_2 = 1$ or 2,000 with or without equal D (crossed area)

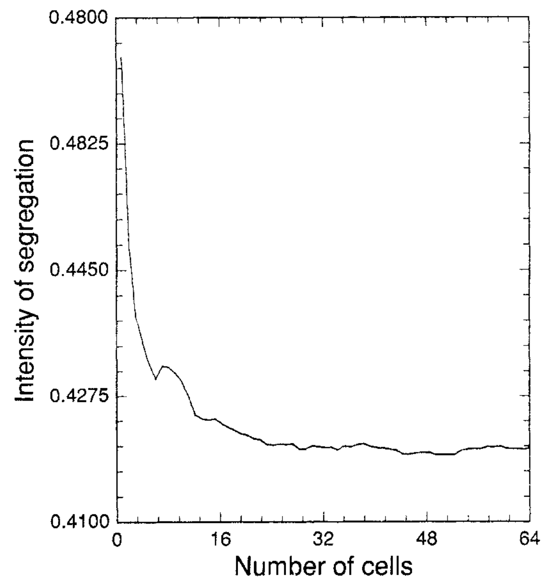

Figure 6. Intensity of segregation variation in the multicell simulation for $k_1/D_1 = 10^{16}$ and $k_1/k_2 = 2{,}000$

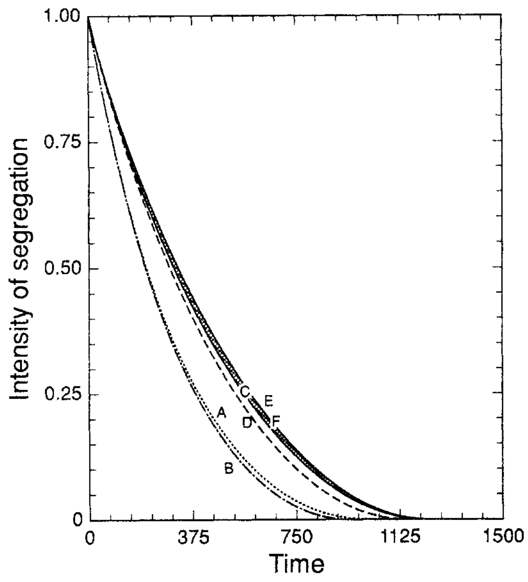

Figure 8. Intensity of segregation variation with time in multicell simulation: same as for Figure 5.

were unexpected as a result of two few mixing interactions in the two-cell model.

A comparison of the $\overline{br}$ covariance results from the two-cell volume averaging, the multirun ensemble averaging, and the multicell volume averaging simulations is shown in Figures 10 through 12 for three levels of k_1/D_1. The comparisons for I_s are not shown because the differences are small. The multicell curves are slightly lower than the two-cell volume-averaging curves and the multirun curves are equivalent. As already noted, the difference is attributed to the interaction effects that the multicell simulations possess while the two-cell and multirun simulations do not. The effect of the additional mixing interactions of the multicell simulation over the multirun and two-cell simulations is greatest at the controlling limits (kinetics and diffusion). At the kinetic-controlled limit of $k_1/D_1 = 10^7$ (Figure 10), the maximum difference between the multicell simulation results and the multirun or two-cell simulation results occurs for equal kinetics (region B). At the diffusion-controlled limit of $k_1/D_1 = 10^{16}$ (Figure 12), the maximum difference between the multicell simulation results and the multirun or two-cell simulation results occurs for a kinetics ratio of 2,000. The smallest difference occurs when both kinetics and diffusion contribute as shown in Figure 11 by region B for equal kinetics and region A for unequal kinetics. The interactions that

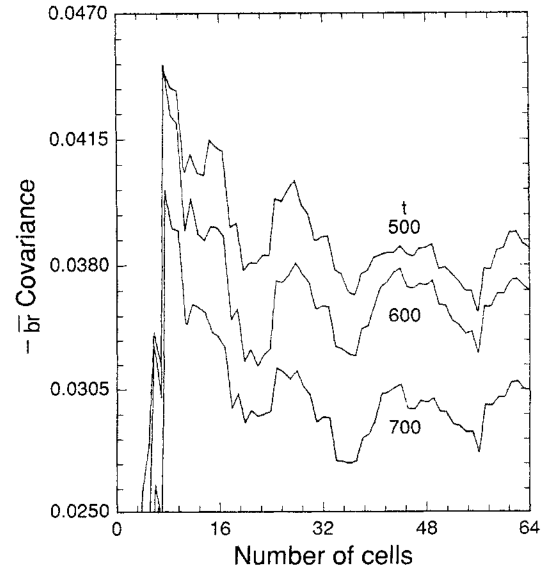

Figure 7. Normalized $\overline{br}$ variation in the multicell simulation for $k_1/D_1 = 10^{16}$ and $k_1/k_2 = 2{,}000$

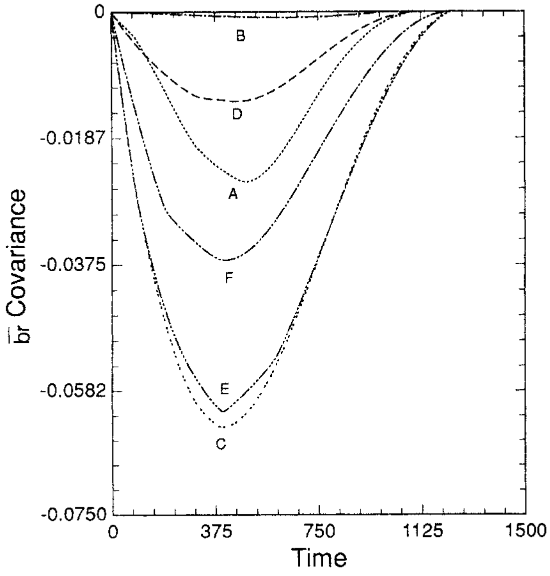

Figure 9. Normalized $\overline{br}$ variation with time in multicell simulation.

For $k_1/D_1 = 10^7$ and $k_1/k_2 = 2{,}000$ (-·-·-) or $k_1/k_2 = 1$ (· · · · ·); for $k_1/D_1 = 10^{10}$ and $k_1/k_2 = 2{,}000$ (-----) or $k_1/k_2 = 1$ (· · · · · ·); for $k_1/D_1 = 10^{16}$ and $k_1/k_2 = 2{,}000$ (··—··—) or $k_1/k_2 = 1$ (-·····-··-)

Table 2. Results from Figures 2 to 9

- Multirun simulation requires only 50 to 100 runs for stable results
- Multicell simulation requires about 64 cells for stable results
- Multirun results in equal but smoother curves compared to the two-cell simulations
- Multicell mixing interactions allows $\overline{br} \rightarrow 0$ as k_1/k_2 increases for diffusion control even though two-cell and multirun techniques do not
- Is decreases slightly as k_1/k_2 increases

are part of the multicell simulation increase the $\overline{br}$ covariance value (toward zero from negative values) over that from the other two methods.

Specific results

The classification of reaction into slow, rapid and very fast by Toor and his coworkers is very useful and is confirmed by the results of the simulation. In Table 3, their suggestions and the simulation results are compared. Only at the high kinetic ratio is the boundary between rapid and very fast slightly different.

The assumption of equal or unequal diffusivities was also tested with the simple model at k_1/D_1 of 10^{13} where the process is expected to be diffusion-controlled. No difference was observed for the kinetic ratio from 1 to 1,000. The multirun results of Figure 4 show the same affect. The result of controlling limits and mechanisms is not new, but it is interesting to verify that a statistical simulation model using randomly selected events can generate these limits. The result suggests that the reaction classification criteria are not sensitive to changes in conditions.

The models were used to determine whether Toor's hypothesis, applied to the first reaction, was satisfied by the statistical program. The results showed that I_s is insensitive to the ratio k_1/k_2 at the two controlling limits. In Figure 8 for the multicell results, compare curves A and B and curves E and F. I_s is relatively insensitive when both mechanisms occur, i.e., in the region between either diffusion or kinetics controlling. The worst case is when k_1/D_1 is 10^{10} (compare curves C and D) with a maximum deviation of 0.03 or about 10%. This shows that I_s is virtually independent of the kinetic rate constants at the controlling limits. When both kinetics and diffusion contribute, the hypothesis could be in error by an amount as large as 10%. This error is not present when only one reaction is involved. For this case, Toor's hypothesis has been shown by experimentation to be valid within about 5%.

It was also observed that Toor's hypothesis applies better at

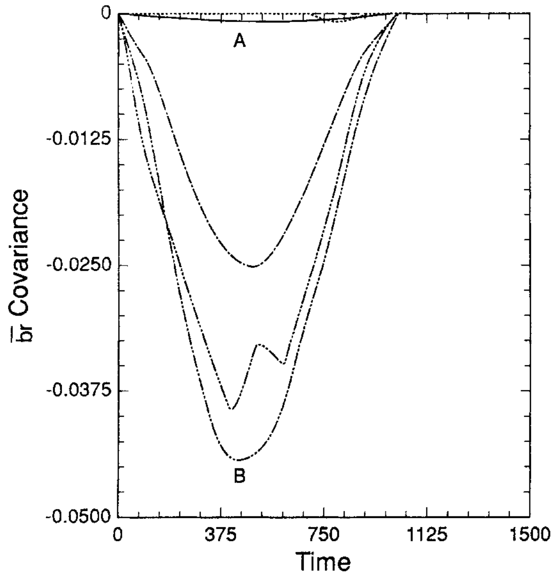

Figure 10. Comparison for the normalized $\overline{br}$ covariance for $k_1/D_1 = 10^7$ and $k_1/k_2 = 2{,}000$: multirun (· · · · ·), multicell (—) and two-cell (-----) models; for $k_1/D_1 = 10^7$ and $k_1/k_2 = 1$: multirun (-· · -·· · ·-), multicell (-······-) and two-cell (-· ··· ·) models

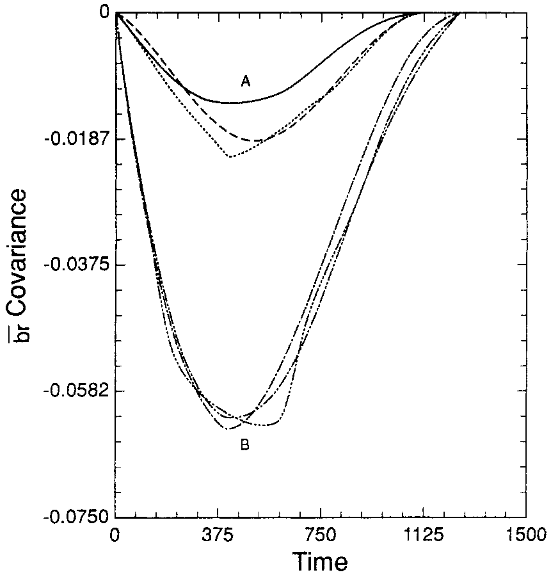

Figure 11. Comparison for the normalized $\overline{br}$ covariance for $k_1/D_1 = 10^{10}$.

Same notation as for Figure 10

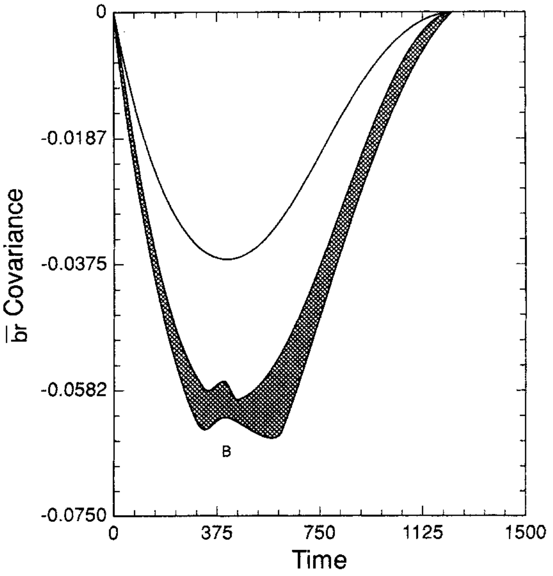

Figure 12. Comparison for the normalized $\overline{br}$ covariance for $k_1/D_1 = 10^{16}$.

Same notation as for Fig. 10

Table 3. Reaction Classification

	Toor	Multicell		Multirun		Two-Cell	
$k_1/k_2 \longrightarrow$		1	2,000	1	2,000	1	2,000
Reaction Class ↓↓	k_1/D_1 Values, m · kmol^{-1}						
Slow	$< 10^7$	$< 10^7$		$< 10^7$		$< 10^7$	
Rapid	$10^7 - 10^{10}$	$10^7 - 10^{10}$		$10^7 - 10^{10}$		$10^7 - 10^{10}$	
Very Fast	$> 10^{10}$	$> 10^{10}$	$> \approx 10^{11}$	$> 10^{10}$	$> \approx 10^{11}$	$> 10^{10}$	$> 10^{13}$

the two controlling limits for the $\overline{br}$ covariance but errors do occur when both mechanisms contribute. The $\overline{br}$ covariance (see Figure 9) is small (< -0.07 when normalized). The error is, of course, a large percentage of the total, since the total is so small. The $\overline{br}$ covariance was always zero for the case of $k_1/D_1 = 1$. This result corresponds to closure 2 of Table 1. The conversion to S for this case was 0.001. This value is close to the experimental results obtained at high Reynolds numbers by Li and Toor (1986).

A summary of effects as determined from the simulation calculations is given in Table 4. The result of increasing the $\overline{br}$ covariance term from a more negative value toward zero is expected. As k_1/k_2 increases, the first reaction becomes much more prevalent and therefore less of the product R is used to produce product S. As R is produced in both types of cells, the instantaneous difference of R between cells should be very small or zero, since there is little consumption of R in forming S. Another expected result is that as the kinetic-controlling limit is approached (k_1/D_1 small), the $\overline{br}$ covariance term should approach zero. In this case, mixing or diffusion occurs quickly in comparison to the reaction. Thus, the amount of R in both types of cells is quickly equilibrated by the relatively fast diffusion.

Simulation results and closure approximations

The statistical simulation can also be used to determine if a particular closure produces the desired values for the $\overline{br}$ covariance. The main interest was to test Eq. 5. Figure 13 shows one comparison between this closure and the simulation results where both kinetics and diffusion are important. Plots for the kinetic and diffusion limits can be found in Heeb (1986) and are not included here as they show similar results. The closure does not reproduce the values at any of the kinetic ratios for the three controlling mechanisms. Another important result is that the closure predicts the opposite response to the kinetic ratio that the simulation values produce. This means that as the kinetic ratio is increased, the simulation results decrease while the closure results increase. This result suggests that the closure is inadequate for use in solving the mixing problem. Table 5 shows the comparison of the two-cell, the multirun and the multicell simulations.

Table 4. Results from Model Simulations

- Unequal diffusivities do not effect I_s or $\overline{br}$ significantly
- Limits are:
  For kinetic control
  $$k_1/D_1 < 10^7$$
  For diffusion control
  $$k_1/D_1 > 10^{10} \text{ for } k_1/k_2 = 1$$
  $$k_1/D_1 > \approx 10^{11} \text{ for } k_1/k_2 = 2{,}000$$
  For both control
  $$10^{10} > k_1/D_1 > 10^7$$
- I_s insensitive to k_1/k_2 ratio
- $\overline{br} \longrightarrow 0$ as k_1/k_2 ratio increases
- $\overline{br} \longrightarrow 0$ as k_1/D_1 decreases

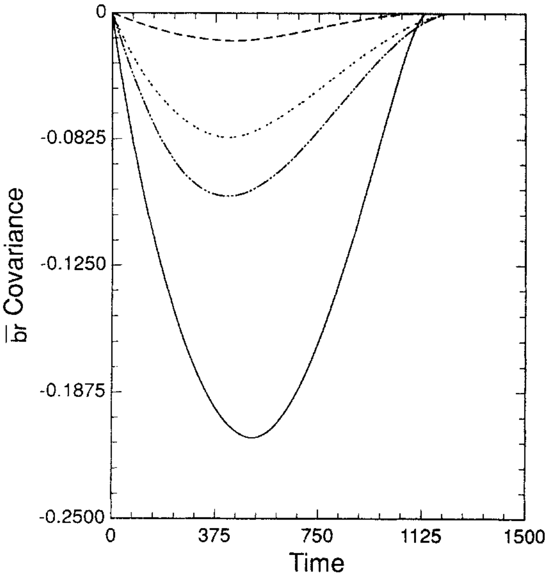

Figure 13. Comparison for the normalized $\overline{br}$ covariance for $k_1/D_1 = 10^{10}$ and $k_1/k_2 = 1$ for closure 1 (·-·-·-·-·); and simulation (·· ·· ··); and for $k_1/k_2 = 2{,}000$ for closure 1 (—) and simulation (-----).

Numerical Integration of the Turbulent Mixing Equations

Integration techniques and equations

The analysis of the turbulent mixing problem with appropriate closures requires integration of the coupled, averaged turbulent component mass conservation equations. For the simultaneous-consecutive reaction system case, a computer program utilizing quadrature was used. For more than two reactions, the solution program utilized Gear's method for stiff partial differential equations. This program was written in ACSL (advanced computer simulation language). Both programs were tested as proposed by Brodkey and Lewalle (1985). The averaged, turbulent component mass conservation equa-

Table 5. Results from Comparing Two-Cell, Multirun and Multicell Simulations

- I_s is slightly lower for the multicell compared to the multirun and two-cell due to Interactions of multicell
- Interaction effect on $\overline{br}$ is largest at kinetic and diffusion controlling limits
- Closure 1 predicts response to k_1/k_2 ratio that is opposite to actual simulation $\overline{br}$ values
- Closure 1 is better for equal kinetics than for unequal kinetics but still does not adequately predict $\overline{br}$ in the simulations (within 100%)

tions consist of the desired closures and the appropriate kinetic expressions. These equations are usually rewritten for fractional conversion and I_s. For the simultaneous-consecutive reaction system given by reaction equation (Eq. 3) and the closure equation (Eq. 5), the following equations are used:

$$\beta \overline{U}_x \frac{dF_A}{dx} = -k_1 A_o (F_A F_B - I_s) \tag{30}$$

$$\overline{U}_x \frac{dF_B}{dx} = (-k_1 A_o - k_2 A_o F_R / F_A)(F_A F_B - I_s) \tag{31}$$

$$\beta \overline{U}_x \frac{dF_R}{dx} = (k_1 A_o - k_2 A_o F_R / F_A)(F_A F_B - I_s) \tag{32}$$

$$\beta \overline{U}_x \frac{dF_S}{dx} = (k_2 A_o F_R / F_A)(F_A F_B - I_s) \tag{33}$$

where the fractional conversion for products R and S are defined as a ratio to A_o as was done by Brodkey and Lewalle (1985).

Discussion

The quadrature program was used to examine the 14 closure equations listed in Table 1. The experimental data of Li and Toor (1986) were used to compare with the closures. The data had a k_1/k_2 ratio of approximately 2,000:1. No data with a ratio of 1:1 were available. The results of the numerical integrations are given in Figures 14 to 16. In these figures, the homogeneous solution refers to the solution of the equations when the intensity of segregation is zero, i.e., when complete mixing is present. The Brodkey-Lewalle closure 1 is inadequate for the range of Reynolds numbers given, although it represents the high Reynolds number regime. Insensitivity to changes in the Reynolds number is a problem with many of the closures. Closure 1 alone is not an adequate representation of the covariance relationship for the entire Reynolds number range for a k_1/k_2 ratio of approximately 2,000:1. No conclusions can be drawn about the adequacy of this closure for different kinetic ratios since experimental data are not available. The statistical simulation results suggest that the closure 1 is not adequate for a kinetic ratio ranging from 1 to 2,000. The result obtained for a kinetic ratio of about 2000:1 is in agreement with the discussion on the failure of this closure to satisfy the molar fluctuation balance equations.

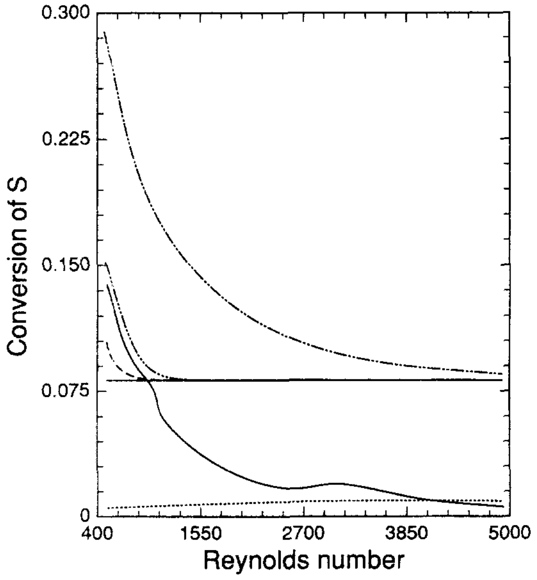

Figure 14. Comparisons of conversion for first five closures and data of Li and Toor (1975).
{1} (· · · · · ·); {2} (-----); {3} and {5} (- · · · - · · · · -); {4} (- · · - · · -); and homogeneous solution at 0.08 (—).

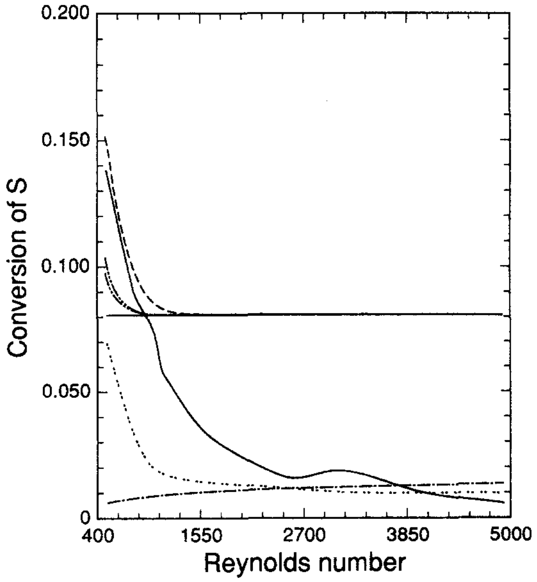

Figure 15. Comparisons of conversion for second five closures and data of Li and Toor (1975).
{6} (· · · · · ·); {7} (-----); {8} (- · - · -); {9} (- · · - · · -); {10} (- · · · - · · · -); and homogeneous solution at 0.08 (—).

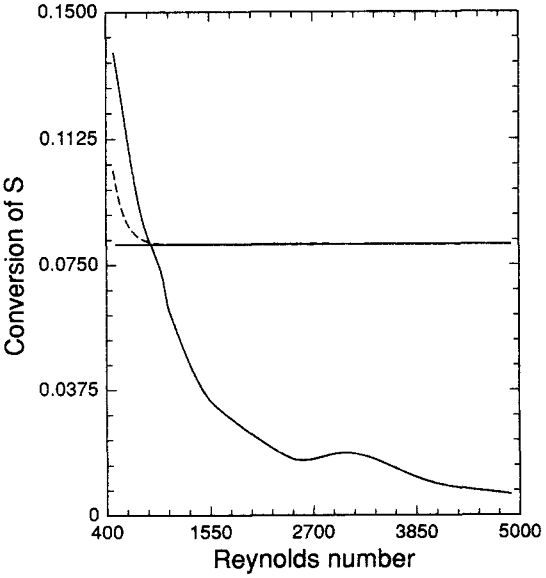

Figure 16. Comparisons of conversion for final closures and data of Li and Torr (1975).
{11}, {12} and {13} (-----); and homogeneous solution at 0.08 (—).

The intensity of segregation used in the numerical integrations was obtained from Singh and Toor (1974). These results were for pure mixing; thus, I_s used in this analysis is the value for mixing alone.

Closure 2 was used to determine if the second covariance term (smaller than $\overline{ab}$) should be zero throughout the reaction. This closure is also inadequate for the range of Reynolds numbers. Ths closure is almost identical to the homogeneous case over most of the range. The difference is negligible if the jet Reynolds number is greater than about 800 (point A). Closure 3, $\overline{B}\,\overline{R}$ and closure 5, the negative of the Brodkey-Lewalle closure, had indistinguishable results. Closure 5 was used to determine if the Brodkey-Lewalle closure could be modified by changing sign. This would describe a premixed system. The results are adequate only at low Reynolds numbers (see region B in Figure 14). Closure 3 cannot be greater than the product of the average components concentrations for an unpremixed system. Thus, the experimental data ranges from slow mixing described by closure 3, the product of the component averages, to fast mixing (high Reynolds numbers) described by closure 1 of Brodkey and Lewalle (1985). The reason that the Brodkey-Lewalle closure 1 describes the high Reynolds number data is because the deviation from segregation is determined from $\overline{ab}$ or I_s and this closure relates to the deviation of $\overline{br}$ from the segregated value of $\overline{B}\,\overline{R}$. Closure 3 is equivalent to the negative of the Brodkey-Lewalle closure as shown in Figure 14. The results imply that the reactor streams can be considered segregated or unpremixed for this low range of Reynolds numbers. The experimental data range from the limit where the covariance is equal to the product of the respective average component concentrations (poor mixing) to the limit where the covariance is related via the Broadkey-Lewalle relationship (fast mixing).

The curves of closure 4, $B_o\overline{R}$, are inadequate for describing the experimental data, but they do produce the proper sensitivity to Reynolds number. This closure is simply the absolute maximum (unrealistic) which a system might attain. This could occur if one component did not react and was not allowed to diffuse and the other component's fluctuations were equated to its average concentration. This limit is unrealistic since the covariance always involves two reactive species and this closure takes one as being inert.

Figure 15 contains five more closure equations that were tested against the experimental data of Li and Toor. Closures 6, 7 and 8 all used the knowledge that the Brodkey-Lewalle closure 1 was adequate at high Reynolds numbers and closure 5 was adequate at low Reynolds numbers. These closures used zero as the connecting value and changed from one closure to another based on either the first or second average Damkoehler numbers. The curves show that the covariance is not simply related through the Damkoehler number.

Closures 9 through 13 involve relating the second covariance term to the first via one of the Damkoehler numbers. There are more than two relationships, since various methods of averaging the concentration terms are available. The results from all of these closures are inadequate. The reasoning behind these closures was that the covariance for the first reaction should be related to the covariance of the second reaction by the ratio of the Damkoehler numbers. The closures that involve just the second reaction's Damkoehler number were chosen because the scale of the reaction system depends on the Reynolds number. This provides some sensitivity to the Reynolds number. The proper scale might produce the correct value for the Damkoehler number to relate $\overline{br}$ to $\overline{ab}$. However, the results of using the various physical scales such as the scalar microscale, macroscale and the Kolmogoroff scale were inadequate. The closures do not predict the experimental data adequately. Not tested were those suggested by Dutta and Tarbell (1989).

Acknowledgment

Acknowledgements are due to the Exxon Educational Research Foundation and the Chemical Engineering Department at the Ohio State University for financial support. Mr. Mike Kukla provided assistance in the experimental portion of this work.

Notation

A, B, C, R, S = concentration of reaction species
a, b, c, r, s = fluctuating components of reaction species
$\langle A \rangle$ = ensemble average of A
A_j = value of A for the jth simulation
A_t = value of A at time t
A_v = volume average of A
A_x = value of A in a cell
D_i = molecular diffusivity of component i, $m^2 \cdot s^{-1}$ or $cm^2 \cdot s^{-1}$
F_i = fractional conversion of component i
I_s = intensity of segregation at a point
J = total number of simulations
k_i = ith reaction's rate constant, $m^3 \cdot kmol^{-1} \cdot s^{-1}$ or $L \cdot mol^{-1} \cdot s^{-1}$
k_i/D_i = reaction to diffusion ratio, $m \cdot kmol^{-1}$ or $L \cdot mol^{-1} \cdot cm^{-2}$
K = parameter in closure 14
N = total number of cells
r_i = instantaneous rate equation for component i
R_i = average rate equation for component i
t = time
T = total time or temperature
U_i = instantaneous velocity in i direction
$\overline{U}_i$ = average velocity in i direction

Greek letters

β = stoichiometric ratio, $\beta = A_o/B_o$
∇ = vector operator

Dimensionless numbers

$N_{Dm_{1,i}}$ = first Damkoehler number for the ith reaction
$N_{Dm_{2,i}}$ = second Damkoehler number for the ith reaction

Subscripts

i = component symbol
o = initial value
s = scalar or segregation
t = time
v = volume
x = x direction

Other symbols

$-$ = averaged quantity
$\langle\,\rangle$ = ensemble average

Literature Cited

Amerja, P. V., M. Singh, and H. L. Toor, "Reactive Mixing in Turbulent Gases," *Chem. Eng. Commun.*, **2**, 115 (1976).

Baldyga, J., and J. R. Bourne, "A Fluid Mechanical Approach to Turbulent Mixing and Chemical Reaction," *Chem. Eng. Commun.*, **28**, 231, 243, 259 (1984).

Brodkey, R. S., *The Phenomena of Fluid Motions*, 4th ed., Addison-Wesley Pub. (1984).

Brodkey, R. S., ed., *Turbulence in Mixing Operations*, "Mixing in

Turbulent Fields," R. S. Brodkey, p. 47; "The non-Premixed Reaction: A + B → Products," H. L. Toor, p. 121, Academic Press, (1975).

Brodkey, R. S., and J. Lewalle, "Reactor Selectivity Based on First-Order Closures of the Turbulent Concentration Equations," *AIChE J.*, **31,** 111 (1985).

David, R., and J. Villermaux, "Micromixing Effects on Complex Reactions in a CSTR," *Chem. Eng. Sci.*, **30,** 1309 (1975).

Dutta, A., and J. M. Tarbell, "Closure Models for Turbulent Reacting Flows," *AIChE J.*, **35,** 2013 (1989).

Ghodsizadeh, Y., and R. J. Adler, AIChE Meeting, New Orleans, LA, Session 61, Paper 61i (1981).

Givi, P., and P. A. McMurtry, "Nonpremixed Reaction in Homogeneous Turbulence: Direct Numerical Simulations," *AIChE J.*, **34,** 1039 (1988).

Heeb, T. G., "Examination of Turbulent Mixing with Multiple Second Order Chemical Reactions by the Statistical Analysis Technique," PhD Diss., Ohio State Univ. (1986).

Klein, J.-P., R. David, and J. Villermaux, "Interpretation of Experimental Liquid Phase Micromixing Phenomena in a Continuous Stirred Reactor with Short Residence Times," *Ind. Eng. Chem. Fund.*, **19,** 373 (1980).

Kosaly, G., "Non-Premixed Simple Reaction in Homogeneous Turbulence," *AIChE J.*, **33,** 1998 (1987).

Lee, J., and R. S. Brodkey, "Turbulent Motion and Mixing in a Pipe," *AIChE J.*, **10,** 187 (1964).

Leonard, A. D., and J. C. Hill, "Direct Numerical Simultation and Simple Closure Theory for a Chemical Reaction in Homogeneous Turbulence," *Lec. Notes in Eng.*, **40,** Springer-Verlag (1989).

Li, K. T., and H. L. Toor, "Turbulent Reactive Mixing with a Series-Parallel Reaction: Effect of Mixing on Yield," *AIChE J.*, **32,** 1312 (1986); also letters on reactor selectivity *AIChE J.*, **32,** 1056 (1986).

Mao, K. W., and H. L. Toor, "A Diffusion Model for Reaction with Turbulent Mixing," *AIChE J.*, **16,** 49 (1970).

———, "Second-Order Chemical Reactions with Turbulent Mixing," *Ind. Eng. Chem. Fund.*, **10,** 192 (1971).

McKelvey, K. N., H. Yieh, S. Zakanycz, and R. S. Brodkey. "Turbulent Motion, Mixing, and Kinetics in a Chemical Reactor Configuration," *AIChE J.*, **21,** 1165 (1975).

Nabholtz, F., R. J. Ott, and P. Rys, "Mixing-Disguised Chemical Selectivities," 2nd Europ. Conf. on Mixing, BHRA Fluid Engineering.

Paul, E. L., and R. E. Treybal, "Mixing and Product Distribution for a Liquid-Phase, Second-Order, Competitive-Consecutive Reaction," *AIChE J.*, **17,** 718 (1971).

Rao, M. A., and R. S. Brodkey, "Mixing and Recycle for Analysis of a Continuous Flow Stirred Tank," *Chem. Eng. Sci.*, **27,** 2199 (1972).

Singh, M., and H. L. Toor, "Characteristics of Jet Mixers-Effect of Number of Jets and Reynolds Numbers," *AIChE J.*, **20,** 1244 (1974).

Toor, H. L., "Turbulent Mixing of Two Species with and without Chemical Reactions," *Ind. Eng. Chem. Fund.*, **8,** 655 (1969).

Ulbrecht, J. J., and G. K. Patterson, eds., "Mixing of Liquids by Mechanical Agitation," "Fundamentals of Turbulent Mixing and Kinetics," R. S. Brodkey, p. 29, Gordon and Breach (1985).

Vassilatos, G., and H. L. Toor, "Second-Order Chemical Reaction in a Nonhomogeneous Turbulent Field," *AIChE J.*, **11,** 666 (1965).

Appendix A: Brodkey-Lewalle Closure as an Extension of Toor's Hypothesis

The mass continuity equations are (one-dimensional system assumed) given by

$$\frac{dC_i}{dt} + U_x\frac{dC_i}{dx} = \frac{d}{dx}\left(D\frac{dC_i}{dx}\right) + r_i \qquad \text{(A1)}$$

The Reynolds-averaged one-dimensional component mass balance equations are

$$\frac{d\overline{C}_i}{dt} + \overline{U}_x\frac{d\overline{C}_i}{dx} + \overline{u_x\frac{dc_i}{dx}} = \frac{d}{dx}\left(D\frac{d\overline{C}_i}{dx}\right) + R_i \qquad \text{(A2)}$$

where R_i is the time-averaged reaction rate at a point in the system. The difference between the one reaction case and the simultaneous-consecutive case is in the reaction terms. The simultaneous-consecutive reaction system as given in Eq. 3 leads to the following reaction terms

$$\text{reaction 1 term} = k_1(\overline{A}\,\overline{B} + a\overline{B} + b\overline{A} + ab) \qquad \text{(A3)}$$

$$\text{reaction 2 term} = k_2(\overline{B}\,\overline{R} + b\overline{R} + r\overline{B} + br) \qquad \text{(A4)}$$

From these, one obtains

$$r_A = -k_1(\overline{A}\,\overline{B} + a\overline{B} + b\overline{A} + ab) \qquad \text{(A5)}$$

$$r_B = -k_1(\overline{A}\,\overline{B} + a\overline{B} + b\overline{A} + ab) - k_2(\overline{B}\,\overline{R} + b\overline{R} + r\overline{B} + br) \qquad \text{(A6)}$$

$$r_R = k_1(\overline{A}\,\overline{B} + a\overline{B} + b\overline{A} + ab) - k_2(\overline{B}\,\overline{R} + b\overline{R} + r\overline{B} + br) \qquad \text{(A7)}$$

$$r_S = k_2(\overline{B}\,\overline{R} + b\overline{R} + r\overline{B} + br) \qquad \text{(A8)}$$

and the averaged terms are

$$\text{averaged reaction 1 term} = k_1(\overline{A}\,\overline{B} + \overline{ab}) \qquad \text{(A9)}$$

$$\text{averaged reaction 2 term} = k_2(\overline{B}\,\overline{R} + \overline{br}) \qquad \text{(A10)}$$

with

$$R_A = -k_1(\overline{A}\,\overline{B} + \overline{ab}) \qquad \text{(A11)}$$

$$R_B = -k_1(\overline{A}\,\overline{B} + \overline{ab}) - k_2(\overline{B}\,\overline{R} + \overline{br}) \qquad \text{(A12)}$$

$$R_R = k_1(\overline{A}\,\overline{B} + \overline{ab}) - k_2(\overline{B}\,\overline{R} + \overline{br}) \qquad \text{(A13)}$$

$$R_S = k_2(\overline{B}\,\overline{R} + \overline{br}) \qquad \text{(A14)}$$

The closure that Brodkey and Lewalle (1985) deduced was utilized in their paper and the results were shown to be qualitatively correct. The procedure to generate this closure is basically the same as given for the $\overline{ab}$ continuity equation. In particular, the continuity equations for the $\overline{b^2}$, $\overline{ab}$, and $\overline{br}$ covariance terms are used to derive the closure needed. The kinetic terms are assumed zero for all k_1 and k_2 following the reasoning of Toor (1969). Thus

$$\overline{ar}\,\overline{B} + \overline{br}\,\overline{A} + \overline{abr} - \overline{ab}\,\overline{B} - \overline{b^2}\,\overline{A} - a\overline{b^2} = 0 \qquad \text{(A14)}$$

$$\overline{b^2}\,\overline{R} + \overline{br}\,\overline{B} + \overline{rb^2} + \overline{br}\,\overline{R} + \overline{r^2}\,\overline{B} + \overline{br^2} = 0 \qquad \text{(A15)}$$

$$\overline{ab}\,\overline{B} + \overline{b^2}\,\overline{A} + \overline{ab^2} = 0 \qquad \text{(A16)}$$

$$\overline{b^2}\,\overline{R} + \overline{br}\,\overline{B} + \overline{rb^2} = 0 \qquad \text{(A17)}$$

$$\overline{a^2}\,\overline{B} + \overline{ba^2} + \overline{ab^2} + \overline{b^2}\,\overline{A} + \overline{ab}(\overline{A} + \overline{B}) = 0 \qquad \text{(A18)}$$

$$\overline{ab}\,\overline{R} + \overline{ar}\,\overline{B} + \overline{abr} = 0 \qquad \text{(A19)}$$

Adding Eqs. A14 and A16 and subtracting Eq. A19 from the result yields

$$\overline{br}\,\overline{A} - \overline{ab}\,\overline{R} = 0 \tag{A20}$$

This equation is the closure that Brodkey and Lewalle (1985) deduced from a two-cell system. Thus their closure is an extension of Toor's invariance hypothesis to include the second reaction. If the closure is inadequate, then Toor's hypothesis is not valid for the second reaction in the two reaction case. The closure was shown to be insufficient for predicting the experimental results of a simultaneous-consecutive reaction system for a jet Reynolds numbers from 500 to 5,000.

Appendix B: Brodkey-Lewalle Closure and Balance Equation

One major problem with the Brodkey-Lewalle closure is that it does not satisfy the overall balance equation for the fluctuating components. The overall mole balance for the reaction system given is

$$A + B + 2R + 3S = A_o + B_o + 2R_o + 3S_o = A_o + B_o \tag{B1}$$

(Assume no R or S initially so $R_o = S_o = 0$.) The overall averaged mole balance is

$$\overline{A} + \overline{B} + 2\overline{R} + 3\overline{S} = A_o + B_o \tag{B2}$$

and the overall fluctuating mole balance is

$$a + B + 2r + 3s = a_o + b_o = 0 \tag{B3}$$

The equations that the closure does not satisfy are equations of the form

$$\overline{\text{Eq. B3} * i} = 0 \tag{B4}$$

such as

$$\overline{a^2} + \overline{ab} + 2\overline{ar} + 3\overline{as} = 0 \tag{B5}$$

These equations are directly from the mole balance equation. Thus, they must be satisfied by any closure presuming to be strictly correct.

Manuscript received June 5, 1990, and revision received Aug. 2, 1990.